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TITLE

POLYOLEFIN MICROPOROUS BREATHABLE FILM HAVING
IMPROVED TEAR, IMPACT STRENGTH, AND SOFTNESS
AND METHOD OF MAKING SAME

INVENTORS

JOHN H. MACKAY
KEVIN A. BRADY

CERTIFICATE OF MAILING

37 C.F.R. § 1.10

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BACKGROUND OF THE INVENTION

This application claims the benefit of U.S. Provisional Patent Application 60/104,455 filed 10/16/98 and U.S. Provisional Patent Application 60/104,948 filed 10/20/98.

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Field

This invention relates generally to a polyolefin microporous breathable film and method of making same. More specifically this invention is directed toward filled polypropylene microporous breathable films having an improved Water Vapor Transmission Rate (WVTR), high tear strength, high dart impact strength, and a soft feel.

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Definitions

As used therein the term "extrusion" is intended to include extrusion, coextrusion, extrusion coating, or combinations thereof, whether by tubular methods, planar methods, or combinations thereof.

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An "oriented" material is defined herein as a material which, when heated to an appropriate temperature above room temperature (e.g., 96°C), will have a free shrink of about 5% or greater in at least one linear direction.

Unless specifically set forth and defined or otherwise limited, the term "polymer" as used herein generally includes, but is not limited to, homopolymers, copolymers, such as, for example, block, graft, random and alternating copolymers,

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terpolymers, etc. and blends and modifications thereof. Furthermore, unless otherwise specifically limited, the term "polymer" shall include all possible molecular configurations of the material. These structures include, but are not limited to isotactic, syndiotactic and random molecular configurations.

5 The term "polyethylene" as used herein refers to families of resins obtained by substantially polymerizing the gas ethylene C_2H_4 . Polyethylenes having densities ranging from about 0.900 g/cc to about 0.935 g/cc are typically called low density polyethylenes (LDPE).

10 The term "linear low density polyethylene" (LLDPE) as used herein for a type of polyethylene to be employed in the film of the invention, refers to the copolymers comprised of a major amount of ethylene with a minor amount of one or more comonomers selected from C_3 to about C_{10} or higher alpha olefins such as butene-1, 4-methyl pentene-1, hexene-1, octene-1, etc. in which the molecules thereof comprise long chains with few side chains or branched structures achieved by low
15 pressure polymerization. The side branching which is present will be short as compared to non-linear polyethylenes. The molecular chains of a linear polymer may be intertwined, but the forces tending to hold the molecules together are physical rather than chemical and thus may be weakened by energy applied in the form of heat. Linear low density polyethylene has a density preferably in the range
20 from about 0.911 g/cc, more preferably in the range of from about 0.912 g/cc to about 0.928 g/cc for film making purposes. The Melt Flow Index of LLDPE

generally ranges from between about 0.1 to about 10.0 grams per ten minutes and preferably between from about 0.5 to about 3.0 grams per ten minutes. LLDPE resins of this type are commercially available and are manufactured in low pressure vapor phase and liquid phase processes using transition metal catalysts. LLDPE is well known for its structural strength and anti-stress cracking properties. Also, LLDPE is known for its favored properties in the heat shrink process, and thus is well suited to make a heat shrinkable film as discussed above. Also, very low density linear low density polyethylenes (VLDPE) may be employed, and such have a density from about 0.010 g/cc to about 0.860 g/cc, or less.

The term "polypropylene" as used herein which polypropylene is a type of polyolefin that may be employed in the film of the present invention, refers to families of resins obtained by substantially polymerizing the gas propylene, C_3H_6 .

By varying the comonomers, catalysts and methods of polymerization, properties such as density, melt index, crystallinity, degree of branching, molecular weight and molecular weight distribution can be regulated over wide ranges. Further modifications are obtained by other processes, such as halogenation, and compounding additives.

Background

Techniques for the preparation of films having good WVTR from highly filled polymers, usually polyolefins, is known. In the past, a combination of a polyolefin,

usually a polyethylene, with a filler, usually CaCO_3 , while very useful and widely used as a film with good WVTR, often, but not necessarily, in combination with nonwoven polymers (for use in diapers, adult incontinence devices, surgical garments, feminine hygiene articles, housewrap composites, protective apparel, roofing materials and the like), has exhibited some limitations that have become well known in the industry.

Among the most serious of the limitations of filled film polyethylene is the extreme difficulty in producing a cost effective lamination between polypropylene nonwoven materials and filled polyethylene breathable films. Traditional attachment techniques such as glue, hot melt, or melt blown adhesive techniques can be used, but these traditional attachment techniques all require the additional cost and process complexity of operating the laminating system as well as the cost of the adhesive itself. The preferred method of heat lamination to attach the filled polyethylene film to the polypropylene nonwoven materials was found to be generally not reliable because of the difference in the melting points of the polypropylene nonwoven material (about 161°C) and the polyethylene film (about 125°C). It has been found that to achieve an adequate lamination bond strength between these two materials, pin holes or damage to the filled polyethylene breathable film occurred at the bond site to the polypropylene nonwoven material.

Prior art polypropylene breathable films, while having lamination advantages over polyethylene films, have been deficient in a number of other performance

categories. Specifically, prior art polypropylene films oriented by traditional Machine Direction Orientation, Transverse Direction Orientation, or Biaxial Orientation (all well known in the art) have exhibited very low tear and impact strength. In addition, the resultant polypropylene films were quite stiff, thus not suitable for providing a comfortable feel against human skin when used for disposables or garments.

For those applications wherein the polypropylene breathable film is not laminated directly to a nonwoven polypropylene, or which by the nature of the product, requires utilization of a hot melt type adhesive gluing system (such as a breathable film diaper backsheet), a polypropylene breathable film provides greater resistance to glue burn through. Thus, the use of a polypropylene breathable film assures product integrity. Also, the use of a polypropylene breathable film enables the use of higher temperature glues, as well as a smaller quantity of glue to achieve adequate product bond strength.

Accordingly, there is a commercial need for a polypropylene microporous breathable film with improved tear strength, improved dart impact strength, as well as a soft feel.

SUMMARY

We have discovered that producing a precursor film from a polypropylene and filler (preferably Calcium Carbonate) blend, then incrementally orienting the precursor film in the machine direction, or the transverse direction, or both, will yield

a reasonably soft film (to the touch) with good dart impact and good tear strength. It was further discovered that adding a minority amount of a low density polyethylene to the polypropylene and filled blend greatly improves extrusion processability. It was further discovered that the addition of a minority amount of an elastomer or a plastomer further improved dart impact strength and tear strength, and contributed to an even softer film feel against human skin. Dart impact strength is approximately double that found in previously available polypropylene breathable films. Machine Direction tear strength is more than triple that found in previously available Machine Direction Oriented and Biaxially Oriented polypropylene breathable films. Transverse Direction tear strength is more than triple that found in previously available Transverse Direction Oriented and Biaxial Oriented polypropylene breathable films. Such dramatic improvements in the physical properties of films are unexpected and surprising.

BRIEF DESCRIPTION OF THE DRAWINGS

A better understanding of the Polyolefin Microporous Breathable Film of the present invention may be had from the drawing figures, wherein:

Figure 1 shows the geometry of interdigitating rollers;

Figure 2 shows a machine direction orientation roller;

Figure 3 shows a transverse direction orientation roller; and

Figure 4 is a cross-sectional of view of an exemplary Water Vapor Transmission Rate (WVTR) test cell.

DETAILED DESCRIPTION

5 Introduction

 This invention concerns certain breathable films made from a polypropylene and filler blend that exhibit high WVTR, and the ability to be drawn down to low basis weights, as well as methods for making same. Particularly useful in the disclosed films and methods is impact copolymer polypropylene.

10 This invention further includes certain polypropylenes, their conversion into fabricated articles such as films, articles made from such films, and applications in which such articles having high WVTR combined with good physical properties such as improved dart impact strength, improved tear strength and soft feel are desirable. The resulting films, and film composites, (including coextruded and laminated films)

15 have combinations of properties which render them superior and unique to films or film composites previously available.

 The filled polypropylene films disclosed herein are particularly well suited for use in producing certain classes of high WVTR films, consumer and industrial articles which use the filled polypropylene films in combination with, for instance,

20 polymeric woven or non-woven materials. Such consumer articles include, but are not limited to diapers, adult incontinence devices, feminine hygiene articles, medical

and surgical gowns and garments, other medical garments, drapes and absorption pads, surgical drapes, industrial apparel, sportswear, building products such as "house-wrap", roofing components, filtration media, controlled atmosphere packaging and the like made using one or more of the films disclosed herein.

5 Additionally the films of the present invention may be used in metallized films with a high WVTR, according to the disclosure of U.S. Patent 5,055,338, which is to be fully incorporated herein by reference in its entirety.

Production of the Films

10 Films contemplated by certain embodiments of the present invention may be made using polypropylene and film processes including, blow molding, casting, or cast melt embossing. The preferred process is a cast melt embossed film process. In extrusion processes, the films of the present invention can be formed into a single layer film, or one layer or more of a multi-layer film or film composite.
15 Alternatively, the polypropylene films described herein can be formed or utilized in the form of a resin blend where the blend components function to modify the WVTR, the physical properties, the draw-down, the sealing, the cost, or other parameters.

Both blend components and the parameters provided thereby will be well
20 known to those of ordinary skill in the art. The breathable films made from the polypropylene and filler blend of the present invention may also be included in

laminated structures. As long as a film, multi layer film, or laminated structure includes one or more polypropylene and filler blend film layers having the WVTR, or draw-down, and the like of the film disclosed herein, such film, multi layer film or laminated structure will be understood to be contemplated as an embodiment of the present invention.

Polyolefin Precursor Film

The polyolefin precursor film component can be any film forming polyolefin blend, as long as the majority of the polyolefin component is a polypropylene. Examples of suitable polypropylene materials are:

Suitable Polypropylenes & Relative Benefits				
Polypropylene Type	Dart Impact Strength	Tear Strength	Softness	Drawdown
Exxon Metallocene Achieve® PD3854	preferred	preferred	preferred	most preferred
Exxon Random Copolymer PP 9263	more preferred	more preferred	more preferred	more preferred
Exxon Impact Copolymer PP 7623	most preferred	most preferred	most preferred	preferred
Exxon Homopolymer PP 1016	preferred	preferred	preferred	preferred

and combinations thereof.

It will be understood that, in general, we contemplate that a large number of polypropylenes will be useful in the techniques and applications described herein.

Filler

Fillers useful in this invention may be any inorganic or organic material having a low affinity for and a significantly lower elasticity than the film used as the polyolefin precursor. Preferably, the filler should be a rigid material having a non-smooth hydrophobic surface, or a material which is treated to render its surface hydrophobic. The preferred mean average particle size of the filler is between about 0.5-5.0 microns for films generally having a thickness of about 1 to about 6 mils prior to stretching.

Examples of the inorganic fillers include calcium carbonate, talc, clay, kaolin, silica, diatomaceous earth, magnesium carbonate, barium carbonate, magnesium sulfate, barium sulfate, calcium sulfate, aluminum hydroxide, zinc oxide, magnesium hydroxide, calcium oxide, magnesium oxide, titanium oxide, alumina, mica, glass powder, zeolite, silica clay, etc. Calcium carbonate (CaCO_3) is particularly preferred for its low cost, its whiteness, its inertness, and its availability. The selected inorganic filler, such as calcium carbonate is preferably surface treated to be hydrophobic so that the filler can repel water to reduce agglomeration. Also, the surface treatment of the filler should improve binding of the filler to the polyolefin precursor while allowing the filler to be pulled away from the precursor film under stress. A preferred coating for the filler is calcium stearate which is both FDA compliant and readily available.

Organic fillers such as wood powder, and other cellulose type powders may be used. Polymer powders such as Teflon® powder and Kevlar® powder can also be used.

5 The amount of filler added to the polyolefin precursor depends on the desired properties of the film including dart impact strength, tear strength, WVTR, and stretchability. However, it is believed that a film with good WVTR generally cannot be produced as is taught herein with an amount of filler less than about twenty percent (20%) by weight of the combined polyolefin/filler blend.

10 The minimum amount of filler (about twenty percent by weight) is needed to assure the interconnection within the polyolefin precursor film of voids created at the situs of the filler – particularly by the stretching operation to be subsequently performed. Further, it is believed that useful films could not be made with an amount of the filler in excess of about seventy percent (70%) by weight of the combined polyolefin/filler composition. It has been found, however, that higher
15 amounts of filler may cause difficulty in compounding and significant losses in strength of the final breathable film. The preferred filler range is about thirty percent (30%) to about seventy percent (70%) by weight, based on the total weight of the combined polyolefin/filler blend. More preferred filler loading will be about forty percent (40%) to about sixty percent (60%) by weight.

20 While a broad range of fillers has been described at a broad range of inclusion parameters based on weight percentages, still other embodiments of the

present invention are contemplated. For instance, fillers with much higher or much lower specific gravity may be included with the polyolefin precursor at amounts outside the weight ranges disclosed. Such polyolefin/filler combinations will be understood to be contemplated as embodiments of our invention as long as the final
5 film, after orientation, exhibits WVTR, or draw-down similar to that described herein.

Film Physical Property Modification

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10 ~~It was also found that the addition of small amounts of low density polyethylene to the polyolefin/filler blend allows film extrusion at higher throughput levels. Low density polyethylene with a Melt Flow Index of about 0.9 to 25.0 grams per ten minutes (being preferred), and a density of about 0.900 to 0.930 may be used.~~

15 Still further improvements in the dart impact strength and tear strength of the film are possible by the addition of plastomers, elastomers, styrenic block copolymers (styrene-isoprene-styrene, styrene-butadiene-styrene), metallocene catalyzed polyethylene, ethylene propylene elastomer polymers, ethylene propylene diene elastomeric polymers or combinations thereof, Ethylene-vinyl-acetate, Ethylene-methacrylate, Ethylene-ethyl-acrylate, and the like, or rubbers. Other commonly available material grades include, but are not limited to, those appearing
20 in the following table.

Property Improvement Materials			
Supplier	Grade	Melt Flow Index	Density
Exxon Chemical	Exact 3139	7.5	.900
Exxon Chemical	Exact 4044	16.5	.895
Exxon Chemical	Exact 9095	2.2	.893
Exxon Chemical	Exact 3131	3.5	.900
Exxon Chemical	Paxon SLX 9106	2.0	.900
Exxon Chemical	Paxon SLX 9101	3.5	.900
Dexco	Vector 4211	13	
Dexco	Vector 4411	40	
Exxon	Vistalon 3708		
Exxon	Vistalon 3030		
Shell	Kraton G1657	8	
Union Carbide	UC 9042	5.1	.900
Union Carbide	UC 1085	0.8	.884

Stretching or Orienting

Final preparation of a breathable film is achieved by stretching the filled polyolefin precursor film to form interconnected voids. Stretching or "orientation" of the film is achieved by incrementally orienting the polyolefin precursor film in the machine direction (MD), transverse direction (TD), or both. Films can be incrementally oriented by a number of mechanical techniques, however, the preferred technique is to stretch the film in the space between pairs of interdigitating rollers, as shown in Figure 1. Therein it may be seen that the film 100 is contracted

by the apex **18** of a plurality of teeth spaced a distance or pitch (W) apart. The apex **18** of each tooth extends into the open space **20** between the teeth on the opposing roller. The amount of interengagement depends both on the tooth depth (d) and the relative position of the rollers.

5 Machine direction orientation is accomplished by stretching the film through a gear-like pair of rollers **16** as shown in Figure 2. Transverse direction orientation is accomplished by stretching the film through a pair of disk-like rollers **26** as shown in Figure 3.

10 The preferred embodiment employs rollers with a tooth pitch, $W = 0.080''$, however a pitch of about $0.040''$ to $0.500''$ is also acceptable. The tooth depth (d), is preferably $0.100''$, however, a tooth depth of about $0.030''$ to $0.500''$ is also acceptable. For the transverse direction orientation rollers, as shown in Figure 3, the depth may be up to about $1.000''$ as mechanical interference is less of an issue when using transverse direction rollers **26**.

15 The depth of interengagement of the roller teeth determines the amount of orientation imparted on the film. A balance must be drawn between the depth of engagement of the roller teeth and the level of filler in the film, as many physical properties of the film are affected as depicted in the following table.

Relationships between process and formulation factors

	Adjust	WVTR	Dart Impact	Basis Weight	CD Tensile	MD Tear
CaCO ₃	Increase	Increase	Decrease			Decrease
MD Orientation	Increase	increase	Decrease	Decrease		Decrease
TD Orientation	Increase	increase	Decrease	Decrease	Decrease	

Properties of Films Produced

WVTR

In an embodiment of the present invention, certain films and articles made therefrom have higher WVTR than previously thought possible. The WVTR of such films should be above about 100 g/m²/24 hr @ 37.8°C, 100% RH, preferably above about 1000 g/m²/24 hr @ 37.8°C, 100% RH, more preferably above about 2000 g/m²/24 hr @ 37.8°C, 100% RH. Some applications benefit from film with up to about 10,000 g/m²/24 hr @ 37.8°C, 100% RH WVTR and above (e.g. garments, etc.).

TEST METHODS

Water Vapor Transmission Rate (WVTR)

Both a Mocon W1, and a Mocon W600 instrument can be used to measure water evaporated from a sealed wet cell at 37.8°C through the test film and into a stream of dry air or nitrogen. It is assumed that the relative humidity on the wet side of the film is near 100%, and the dry side is near 0%. The amount of water vapor in the air stream is precisely measured by a pulse modulated infra red (PMIR) cell. Following appropriate purging of residual air, and after reaching a steady state water vapor transmission rate, a reading is taken. WVTR of the test films are reported at Grams of Water/Meter²/Day @ 37.8°C. The output of the unit has been calibrated to the results obtained with a film of known WVTR. Typically, a Celgard 2400 film having a WVTR of 8700 g/m²/day @ 37.8°C is used as a reference. The testing protocols are based on ASTM 1249-90. The diagram depicted in Figure 4 illustrates the basic operation of the Mocon units.

Mocon W1

As illustrated generally by reference to Figure 4, the Mocon W1 has a single test cell and an analog chart recorder. Air is pumped through a desiccant dryer, then through the test cell, and then past the PMIR sensor. A five-minute purge of residual air is followed by a six-minute test cycle with controlled air flow. The result is a steady state value for WVTR. The purge and test cycles are controlled

manually. The unit is calibrated to a film with a known WVTR every twelve hours. Calibration results are control charted and adjustments are made to the instrument calibration accordingly.

5 Mocon W600

10 The Mocon W600 has six measurement cells with PMIR data fed into a computer. Nitrogen is fed through a desiccant dryer, then through the active test cell, then past the PMIR sensor. In addition to data compilation, a computer controls test cycle sequencing. All measurement cells are purged simultaneously for an eight-minute period. This is followed by an eight-minute test cycle for each of the six measurement cells. Total testing time is fifty-six minutes. Two of the six measurement cells always measure reference films with a known WVTR.

15 EXAMPLES

Example 1. Experimental grade 300-11-1

A blend of 52% ECC FilmLink 400 CaCO_3 was combined with 48% Exxon PD 7623 Impact Copolymer Polypropylene. The film was oriented off line with interdigitating rolls of 0.100" pitch. The MD depth of engagement was 0.030", and the TD depth of engagement was 0.019".

Example 2. Experimental grade 400-4-1

A blend of 52% ECC FilmLink 400 CaCO_3 was combined with 40% Exxon PD 7623 Impact Copolymer, 2% Exxon LD-200.48, 6% Exxon SLX9101. The film was oriented in interdigitating rolls of 0.080" pitch. The MD depth of engagement was 0.028", and the TD depth of engagement was 0.034".

Example 3. Experimental grade 500-9-3

A blend of 55% ECC FilmLink 400 CaCO_3 was combined with 31% Exxon PD 7623 Impact Copolymer, 4% Exxon LD-200.48, 2% Ampacet 110131 TiO_2 , concentrate, and 8% Exxon Exact 3131. The film was oriented in interdigitating rolls of 0.080" pitch. The MD depth of engagement was 0.021", and the TD depth of engagement was 0.037".

The following table demonstrates the absolute values of tear strength and dart impact strength of the film produced in three examples.

Table of Example Film Properties

	Example 1	Example 2	Example 3
Grade Number	300-11-1	400-4-1	500-9-3
Basis Weight (gm/sqm)	41.0	40.6	40.3
WVTR (gm/sqm/day)	1457	1462	1400
Dart Impact Strength (gm)	210	315	315
MD Ultimate (gm/in)	625	609	604
MD Elongation (%)	423	482	448
TD @ 5% (gm/in)	231	151	140
TD Ultimate (gm/in)	367	501	440
TD Elongation (%)	410	464	398
Light Transmission (%)	45	43	39
MD Elmendorf Tear Strength (gm)	79	195	198

Based on the foregoing, the films produced by the disclosed method have physical properties as described below:

WVTR (gm/sqm/day)	100 – 10,000
Dart Impact Strength (gm)	100 – 300 grams
MD Elongation (%)	150% – 550%
TD Elongation (%)	150% – 550%
MD Elmendorf Tear Strength (gm)	20 – 300 grams

Changes and modifications in the specifically described embodiments can be carried out without departing from the scope of the invention which is intended to be limited only by the scope of the appended claims.